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<b>(54) Title:</b> IMPROVED OIL AND FRACTIONATION PROCESS  <b>(57) Abstract</b>  Vegetable oils, that are visibly clear at room temperature and that have a Mettler drop point below 20 °C comprise combined levels of C <sub>16:0</sub> and C <sub>18:0</sub> of less than 9 wt%. The oils display AOM values of at least 150 hrs. Addition of natural oxidants improves the AOM value of the oils.		

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IMPROVED OIL AND FRACTIONATION PROCESSBackground of the Invention

5 Oils, particularly those which are to be used in foods,  
must exhibit a degree of flavour stability appropriate to  
the conditions of their use and storage. In general,  
flavour stability is directly related to oxidative  
stability. Since oxidation often occurs in oils after they  
10 have been used in the production of foods, oils having a  
high degree of oxidative stability are in demand. Oxidative  
stability tends to be decreased by the presence of poly  
unsaturated moieties in the oils, such as fatty acid  
moieties having two or three sites of unsaturation. Tri-  
15 unsaturated fatty acids are especially prone to oxidation.

Another desirable characteristic for oils to be used in  
foods and other applications is clarity at room  
temperature. An oil which is not clear at room temperature  
20 will not be as readily accepted and used as one which is  
clear. Therefore, it has been desirable to develop an oil  
which satisfies the twin requisites of high oxidative  
stability and clarity at room temperature.

25 It has been found, unfortunately, that often it is not  
possible readily to filter out crystals which impair the  
clarity of lightly hydrogenated canola oil, unless the  
canola oil is hydrogenated to such an extent that low  
yields (50% or below) of high stability clear oil are  
30 obtained.

Du Pont WO 92/03919 discloses a canola seed with a maximum  
content of FDA saturates of 5.9%. The seed has an oleic  
acid content of 69-80%.

35

WO 90/10380 discloses a homogeneous assemblage of mature  
rapeseeds having an oleic acid content of at least 79 wt.%

with respect to total fatty acids and an erucic acid content of not over 2 wt.%. The seeds are said to give a vegetable oil having high heat stability. The vegetable oil may be used as a frying oil.

5

EP 323,753 discloses mature rapeseeds having by weight total fatty acid content a high oleic acid content of at least 79% and not more than 2% erucic acid. The produced oil is said to have increased heat stability.

10

"CANOLA OIL Properties And performance" publication No. 60 (Oct. 1982) states that canola oil is a natural salad oil that remains clear and liquid at refrigerated conditions. It is said that canola oil may be lightly hydrogenated to improve flavour stability and that higher melting triglycerides which may be formed can be removed by winterizing out to insure that the oil remains clear under refrigerated conditions. It states that by slowly cooling an oil to around 2-5°C, the high melting triglycerides form large, easily filtered crystals which can be removed in a filter press.

Fick US Patent No. 4,627,192 discloses a sunflower seed having an oleic acid content of 80% or greater. Fick US Patent No. 4,743,402 discloses a high oleic sunflower oil.

Trisun® technical Bulletin HS-500 from SVO Enterprises of Eastlake, Ohio discloses a lightly hydrogenated, ultra high stability sunflower oil said to be a true 500 AOM hour oil. HS-500 is said not to require solvent fractionation to achieve its high stability. An iodine value of 76, and AOM stability of 530 hours, and a melting point of 18°C are reported. The SFI at 10°C is said to be 2-10 and the fatty acid distribution is reported as C<sub>16:0</sub>, 4%, C<sub>18:0</sub>, 6%; C<sub>18:1</sub>, 87%; C<sub>18:2</sub>, <1%; C<sub>20:0</sub>, 1%; C<sub>20:1</sub> -; C<sub>22:0</sub>, 1%. 0.2% tocopherol natural antioxidant is included.

FR 2,617,675 discloses groundnut seed with an oleic acid content of 74-84% and a linoleic acid content about 2-8%. The low linoleic acid content is said to ensure high storage stability.

5

WO 91/11906 discloses safflower seeds having an oleic or linoleic acid content of at least 80%.

#### Summary of the invention

10

The present invention is directed to an oil which is clear at room temperature and which possesses a high degree of oxidative stability, and to a process for preparing the oil. The oil of the invention may be prepared by obtaining  
15 a vegetable oil, preferably from a high oleic canola seed, e.g. as those disclosed in DU Pont WO 92/03919, particularly Examples 6 and 7, especially Tables IX, X, and XI, and lightly hydrogenating the oil to an iodine value in the range of from about 82 to about 72, preferably about 80  
20 to 76, and particularly from about 77 to 79. Subsequently, the hydrogenated product is fractionated, preferably by dry fractionation, to provide in good yield a high stability oil which can be filtered to remove any crystals present whereby to obtain an oil which is clear at room  
25 temperature.

The above process results into an oil having a low Mettler drop melting point of, say below 15°C and low total C<sub>16:0</sub> and C<sub>18:0</sub> saturates of, for instance under 9% by weight.  
30 The high oxidative stability may be manifested in a minimum AOM of 250 hrs, preferably greater than 250 hrs and most preferably greater than 300 hrs.

Yields of greater than 50% by weight and especially 65% or  
35 more by weight based on the weight of the starting hydrogenated oil are possible with the present invention.

The oil need not include any added antioxidants to achieve the indicated AOM values.

According to another embodiment of the present invention  
5 the invention is directed to an oil which is essentially clear at room temperature and which possesses a high degree of oxidative stability, and to process for preparing the oil. This oil may be prepared by lightly hydrogenating a vegetable oil, preferably an oil obtained from a high oleic  
10 canola seed, to an iodine value in the range of from about 85 to about 75, preferably from about 79 to 82.

Despite its high oxidative stability, this oil has a melting point (Mettler drop point) below 20°C, preferably  
15 below 18°C and most preferred below 15°C. The oxidative stability of the oil is reflected in AOM values of over 150 hours, especially over 200 hours, and most preferably greater than 250 hours. The oil preferably includes low amounts of C<sub>16</sub> and C<sub>18</sub> saturates, namely under about 8.5%  
20 combined C<sub>16:0</sub> and C<sub>18:0</sub>.

The oil of this embodiment is preferably not fractionated. A particularly advantageous feature of this embodiment is the development of an oil which is not fractionated yet  
25 which possesses a high oxidative stability, e.g. AOM greater than 150 hours, and at the same time has a melting point of under about 20°C.

According to another embodiment of the present invention  
30 the invention is directed to an oil which possesses a high degree of oxidative stability, and to a process for preparing a preferred oil. Preferably, the oil is essentially clear. This oil is prepared by combining a partially hydrogenated high oleic canola oil with  
35 tocopherols, especially delta tocopherols, or other natural antioxidants. An especially preferred oil is prepared by lightly hydrogenating an oil obtained from a high oleic

canola seed to an iodine value in the range of from 85 to 75, preferably from 79 to 82, and adding to the oil thus prepared natural antioxidants, particularly tocopherols and especially delta tocopherols.

5

This embodiment is also directed to lightly hydrogenated canola oils having a high proportion of oleic acid moieties in the triglycerides and to which natural antioxidants such as delta tocopherols have been added. The invention is also directed to the oil made by the process described above. Other antioxidants which may be used include alpha tocopherols, gamma tocopherols and rosemary oleoresin.

Those oils preferably include less than 30 wt% combined C<sub>16:0</sub> and C<sub>18:0</sub> saturated fatty acids plus trans fatty acids, especially less than 25% combined C<sub>16</sub> and C<sub>18</sub> saturated fatty acids plus trans fatty acids.

#### Detailed Description of the Invention

20

Oils may be obtained from seeds by well-known techniques. The starting oil is preferably a vegetable oil and most preferably a high oleic canola oil. Canola oil is low erucic acid rapeseed oil. Preferred high oleic canola oil starting materials are seeds disclosed in Du Pont WO 92/03919, the disclosure of which is incorporated by reference herein. Examples of seeds which might be used include, but are not limited to, A128.3, A129.5.3, M3028-10 in Example 6, and M3062.8 and A133.1.8 in Example 7. Also, it is contemplated that the oil of other high oleic seeds such as those of EP 323,753 to Allelix Inc. can be employed.

The preferred starting canola oil is derived from rapeseed and preferably has a C<sub>18:1</sub> percentage of from 65 to 95% by weight, a C<sub>18:2</sub> of from 5 to 20% by weight, a C<sub>18:3</sub> content

of from 0.5 to 9% by weight and an iodine value of from 95 to 115.

Preferably, the starting oil has a  $C_{18:1}$  value of greater  
5 than about 70% by weight, a  $C_{18:2}$  value of less than 15% by weight, a  $C_{18:3}$  value of less than 7% by weight and an iodine value of less than 105, preferably less than 100.

The first step in the process of obtaining the present oils  
10 is hydrogenation. The starting oils are hydrogenated to an iodine value of between about 72 and 85, preferably from 80 to 76, especially from 77 to 79. Preferably, the hydrogenation occurs at a temperature of from about 138°C to 177°C. Standard batch hydrogenation equipment featuring  
15 internal steam heating and water cooling may be used. Selective nickel supported catalysts such as G-95 available from United Catalyst in Louisville, Kentucky, Pricat 9920 available from Unichema, Emmerich, Germany and Calcicat 472 from Mallinkdrodt of Erie, Pa. may be used.

20 Preferably, the starting oil is hydrogenated to a refractive index of appropriate value to obtain the desired iodine values. A refractive index of approximately 1.495 at 48°C would be an appropriate target.

25 The oil obtained may include trans fatty acid moieties, preferably at a level of greater than 16% by weight, especially greater than 22% and most particularly at levels of from about 25 to 30%.

30 After the oil has been lightly hydrogenated it can be dry fractionated or winterized. The hydrogenated oil is melted and pumped into a slowly agitated winterization cell. While a horizontal cell is used in the Example below, vertical  
35 winterization cells could also be used. The liquid oil is then slowly cooled by an appropriate means to approximately 14°C. Preferably, appropriate care is taken not to cool the



batch to under about 10°C. After the desired temperature of 14°C is obtained, the slowly agitated mixture is maintained at 14°C for about two hours to enable the crystallization of the solid triglycerides to be completed and to avoid a post crystallization in the filtered product. The solid crystals are then removed by filtration using an appropriate filter system such as a Bird Young rotary filtration unit.

10 Winterization yields may be in the order of 65% to 80%.

After winterization, the oil is deodorized under standard deodorization conditions for canola oil. Typically, the oil is heated to 243 to 260°C under a reduced pressure of from about 3-7 mm Hg and steam is passed through.

The filtered liquid oil of the invention so obtained includes no visible solids at 21°C and possesses a high oxidative stability of over 250 hours AOM as measured by the American Oil Chemists Society AOM Method Cd 12-57. The filtered liquid oil is preferably clear. Preferred liquid oils according to the invention have an SFI at 10°C of 1.8 or less, especially 1.5 or less.

25 According to a particularly advantageous feature of the present invention no winterization or other fractionation of the oil is applied to obtain an essentially clear oil with high oxidative stability. After the oil has been lightly hydrogenated, it is filtered to remove the catalyst, and deodorized under standard conditions for canola oil. Small amounts of citric acid dissolved in propylene glycol may be added prior to filtration to help in the removal of nickel catalyst and iron from the hydrogenated oil. Typically, the oil is heated to 232 to 260°C under a reduced pressure of from about 3-7 mm Hg and steam is passed through for deodorization.

The oil thus obtained is essentially clear at room temperature. That is, at room temperature the oil includes small amounts of scattered crystals.

- 5 According to another embodiment of the invention an oil is obtained by adding delta tocopherols or other natural antioxidants to canola oil. Delta tocopherols are preferred. Preferably, the delta tocopherol mixtures are added at from 0.1 to 0.5 weight %. Other antioxidants
- 10 contemplated for use herein include alpha tocopherols, gamma tocopherols mixtures of two or more tocopherols and rosemary extract. Eisai USA, Inc. of Teaneck, N. sell a delta tocopherol concentrate having 85.1% tocopherol comprising 0.6% alpha tocopherol, 5.4% gamma tocopherol and
- 15 94% delta tocopherol identified as E-Mix D. A mixture of 10.2% alpha tocopherol, 61.6% gamma tocopherol and 28.2% delta tocopherol in soybean oil (70% tocopherol; 30% soybean oil) is sold as Tenox GT-2 by Eastman Kodak. A rosemary oleoresin from which chlorophyll and camphor have
- 20 been substantially removed dissolved in vegetable oil and mono- and di-glycerides is sold as Herbalox<sup>®</sup> Seasoning Type O by Kalsec, Inc. of Kalamazoo, Michigan. The above and other products are contemplated for use herein.
- 25 The process for preparing the preferred oils comprises the same light hydrogenation of the starting high oleic canola oil to an iodine value of between 75 and 85, especially between about 79 and 82, as described before. Preferably, the hydrogenation occurs at a temperature of from 138°C to
- 30 177°C. Standard batch hydrogenation equipment featuring internal steam heating and water cooling may be used. Selective nickel supported catalysts such as G-95 available from United Catalyst in Louisville, Kentucky, Pricat 9920 available from Unichema, Emmerich, Germany and Calcicat 472
- 35 from Mallinckrodt of Erie, Pa, may be used. Preferred catalysts would be selective catalysts.

Delta tocopherols are added to the oil at some stage during the processing, preferably after the oil has been deodorized. Although the invention encompasses addition of natural antioxidants to high oleic canola oils, it has been found that, surprisingly, the addition of natural antioxidants has a markedly increased effect on a high oleic canola oil which has been lightly hydrogenated in accordance with the preferred process compared to the effect seen when delta tocopherols or other natural antioxidants are added to other oils including other non-hydrogenated high oleic canola oils. Best results are obtained with the addition of delta tocopherols.

The natural antioxidants is preferably added at a level of 0.1 wt% to 0.5 wt%, particularly 0.1 to 0.4 wt% and especially from 0.1 to 0.2 wt% of the antioxidants mixture based on the weight of the oil. This amounts to about 800 ppm to 1750 ppm tocopherols on a 100% basis. The oil of the invention is preferably essentially clear at room temperature. That is, at room temperature the oil includes small amounts of scattered crystals.

Unless indicated otherwise, AOM determinations herein are made in accordance with AOCS AOM method Cd 12-57. Unless otherwise indicated or otherwise required by the context, iodine values refer to calculated iodine values.

The oils of the invention may be used, for example, in the preparation of foods. Examples include uses as ingredients, as coatings and as frying oils. Foods in which the oil may be used include, but are not limited to, confectionery products, syrups and toppings, sauces and gravies, soups, batter and breading mixes, baking mixes and doughs.

All percentages given herein are by weight unless stated otherwise or unless the context clearly requires otherwise. All references to drop point or melting points are to the

Mettler drop point method, AOCS Dropping point C<sub>c</sub> 18-80 unless stated otherwise or the context clearly requires otherwise.

5

EXAMPLE I

The oil labelled high oleic A having the fatty acid and other characteristics provided in Table 1 below was hydrogenated, in accordance with the following procedure.

10

TABLE 1

Fatty acid compositions canola oils		
Hi oleic A		
15	16:0	4.0
	16:1	0.4
	17:0	0.3
	18:0	2.3
	18:1	75.3
20	18:2	9.1
	18:3	5.4
	20:0	0.8
	20:1	1.8
	22:0	0.4
25	22:1	0.3
	CALCD IV	96.1
	FFA	0.07
	COLOR	1.1 R
30	RANCIMAT 130C	0.85
	AOM	PASS 20
		FAIL 25

The hydrogenation was conducted in a standard batch  
 35 hydrogenation reactor at a pressure varying between 1.14 and 1.07 Bar. Five batches were hydrogenated. The oil was heated to an initial gassing temperature of 149°C and the

hydrogenation was conducted over a period of approximately 1 hour and 5 minutes. The temperature at the end of hydrogenation was 180°C. The nickel catalyst used was F-95. The oil was hydrogenated to a refractive index of 1.495 at 5 48°C. 20-40 ppm citric acid dissolved in propylene glycol was added to the hydrogenated oil prior to filtration. The citric acid was utilized to help remove nickel and iron from the oil. An analysis of the hydrogenated batches of oil is given in Table 2.

**TABLE 2**  
**HYDROGENATION**

		A-82	A-83	A-84	A-85	A-86
	RI	1.495	1.494	1.494	1.493	1.495
5	Color	0.5 Red	0.8 Red	0.8 Red	0.5 Red	0.4 Red
	MDP C	20	21.3	20.6	24.5	18.5
	F	68	70.3	69	76.1	65.3
	IV	78.9	79.4	80	78	78.8
	Trans	28.9	29.9	28.9	33.1	29.5
10	SFI 10°C	8.1	10.3	9.4	15.4	9.5
	21°C	1.4	2.1	2	4.4	2
	27°C	0.6	1.2	1	2.2	0.6
	FAC 16:0	3.9	NA	4.2	3.9	4
	16:1	0.6		0.7	0.6	0.6
15	17:0	0.3		0.3	0.2	0.2
	18:0	5.5		5.6	6.4	5.5
	18:1	84.1		84.4	84.3	84.7
	18:2	2.2		1.7	1.5	1.7
	18:3	0.1		0.1	0.1	0.1
20	20:0	0.85		0.8	0.9	0.9
	20:1	1.7		1.5	1.5	1.6
	22:0	0.4		0.4	0.2	0.3
	22:1	0.3		0.2	0.2	0.1
	CALCD IV	78.5		77.8	77.2	77.9
25	Rancimat 130°C	16.8	19.5	18.3	18.4	18.8

MDP= Mettler Dropping Point

Winterization

	Run Number	17	18	19	20
5	Temperature°C	14			
	Yield	70	65*	65*1	65* 70

\* Due to filtration difficulties, cells were partially filtered to about a 50% yield each. The unfiltered contents were then combined and subsequently winterized to the 65% yield shown.

The hydrogenated oils were melted and pumped to winterization cells. The batches were slowly cooled to 14°C and held at 14°C for 2 hours. Filtering was conducted using a Bird-Young filter.

The winterized high oleic canola oil was deodorized under standard canola deodorization conditions and combined in a tank and then packed in a drum. The winterized oil was visibly clear at 21°C. Characteristics of the hydrogenated and winterized oil are provided in Table 3.

TABLE 3

## DRUM

5	Color	.5 R
	FFA	0.03
	Flavour	Bland
	PV	0.2
	MDP C	13.5
10	F	56.3
	IV	-
	TRANS	28.9
	FAC 16:0	3.6
	16:1	0.6
15	17:0	0.3
	18:0	4.7
	18:1	85.5
	18:2	2.1
	18:3	0.1
20	20:0	0.8
	20:1	1.7
	22:0	0.4
	22:1	0.2
	CALCD IV	79.4
25	RANCIMAT 130°C	20 HRS
	AOM	373 hours



EXAMPLE II

The high oleic canola oil having the fatty acid composition and other characteristics provided in table 4 below was hydrogenated in accordance with the following procedure.

TABLE 4

## FATTY ACID COMPOSITION STARTING CANOLA OIL

10

15

20

16:0	3.6
16:1	0.2
17:0	0.2
18:0	2.4
18:1	76.1
18:2	8.2
18:3	5.9
20:0	0.8
20:1	1.6
22:0	0.5
Calculated IV	96.4

Rancimat 130°C

1.52 hrs

RI at 48°

1.53

25

The hydrogenation was conducted in a reactor at a pressure varying between 1.14 and 1.07 Bar. The reactor was pre-heated to an initial gassing temperature of 149°C (reactor gauge temperature) over a period of approximately  $\frac{1}{2}$  hour.

30 The maximum temperature was 171°C. The temperature at the end of hydrogenation was 170°C. The batch was hydrogenated to a refractive index of 1.50 at 48°C. G-95 catalyst was

employed. The batch was filtered to remove nickel catalyst. 20-40 ppm of citric acid dissolved in propylene glycol was added prior to filtration. The citric acid was utilized to help remove nickel catalyst. The filtered oil was pumped to  
5 a tank and deodorized. Table 5 gives analytical data for the hydrogenated oil.

TABLE 5

	Sample	Reactor filtered from QC	Tank 881 Deod
	Rancimat		
5	130°	12.6	17.5
	140°		9.4
	AOM		259 hrs
	FFA		0.03
	Colour	0.3 R	0.3 R
10	RI QC	1.49	1.50
	IV	83.7	81.5
	DP deg. C.	12.6	13.9
	Trans		24.2
	PV		0.2
15	FAC 16:0	3.7	3.7
	16:1	0.4	0.4
	17:0	0.2	0.1
	18:0	4.1	4.0
	18:1	85.0	85.7
20	18:2	3.2	2.9
	18:3	0.2	0.1
	20:0	0.8	0.7
	20:1	1.6	1.6
	22:0	0.4	0.4
25	22:1	-	-

As can be seen from Table 5, the deodorized oil has an AOM of over 250 hours and a Rancimat value of 17.5 at 130°C in contrast to the starting Rancimat value at 130°C of 1.52 hours. In addition to having excellent oxidative stability, the oils of the invention are essentially clear at room temperature. That is, at room temperature the oil includes small amounts of scattered crystals. The essential clarity of the oil is reflected in the low melting point and low C<sub>16</sub> and C<sub>18</sub> saturates.

10

After deodorization the oil was packaged in drums.

#### EXAMPLE III

15 The high oleic canola oil having the fatty acid and other characteristics provided in Table 6 below was hydrogenated in accordance with the following procedure.

TABLE 6

## FATTY ACID COMPOSITION STARTING CANOLA OIL

5	16:0	3.6
	16:1	0.2
	17:0	0.2
	18:0	2.4
	18:1	76.1
10	18:2	8.2
	18:3	5.9
	20:0	0.8
	20:1	1.6
	22:0	0.5
15	Calculated IV	96.4

Rancimat 130°C

0.73 hrs

RI at 48°

1.53

20 The hydrogenation was conducted in a reactor at a pressure varying between 1.14 and 1.07 Bar. Samples were taken from different hydrogenation batches. Each sample was laboratory filtered and laboratory deodorized. The reactor was pre-heated to an initial gassing temperature of 149°C. The

25 maximum temperature was 177°C. G-95 catalyst was employed. Each sample was filtered to remove nickel catalyst. 20-40 ppm of citric acid dissolved in propylene glycol was added prior to filtration. The citric acid was added to help remove nickel catalyst. Each filtered oil was laboratory

30 deodorized. An analysis of the hydrogenated samples is given in Table 7. The samples were taken at different refractive indexes at 48°C. Sample 1 was taken at a RI of

1.51 at 48°C, Sample 2 was taken at an RI of 1.50 at 48°C and Sample 3 was taken at an RI of 1.50 at 48°C.

TABLE 7

		Sample 1	Sample 2	Sample 3
5	RI	1.51	1.50	1.50
	DP C	3.5	8.7	12
	F	38.3	47.66	53.6
	IV	87.8	84	81.7
	TRANS	11.7	16.3	19.4
10	SFI			
	10°C	0	0.6	2
	21°C	0	0	0.4
	27°C			
	33°C			
15	FAC			
	16:0	4.2	4.2	3.9
	16:1	0.6	0.6	0.4
	17:0	0.4	0.4	0.2
	18:0	3.2	3.5	4.1
20	18:1	79.8	83.1	85.3
	18:2	7	4.5	2.7
	18:3	1.3	0.2	0.1
	20:0	0.8	0.9	0.9
	20:1	1.7	1.8	1.7
25	22:0	0.4	0.4	0.4
	22:1	0.4	0.3	0.5
	CALCD IV	86	82	80
	OM	FAIL 30	PASS 150	PASS 210
	RANCIMAT 130°C	6.17	10.8	14.4
30	PLUS .125% GT-2 RANCIMAT	7.07	12.5	19.5
	AOM	PASS 110 HRS	190 FAIL 190	350 400
	.25% GT-2 RANCIMAT	8.4	13.6	24.4
	AOM	PASS 110 HRS	PASS 190 FAIL 230	400
	.1% DELTA T RANCIMAT	6.07	14.6	21.2
35	AOM	PASS 110 HRS	PASS 190 FAIL 230	350 400

(Table 7 - continued)

	.2% DELTA RANCIMAT	10	17.4	26.2
5	AOM	PASS 110 HRS	PASS 270 FAIL 310	400
	.1% KALSEC RANCIMAT	6.7	13.6	18.7
	AOM	PASS 90 HRS FAIL 110 HRS	PASS 190 FAIL 230	250 400
10	.2% KALSEC RANCIMAT	7.08	14.2	21.4
	AOM	PASS 110 HRS	PASS 270 FAIL 310	350 400
	.4% KALSEC RANCIMAT	9.63	17.2	25.2
15	AOM		PASS 310	

Characteristics of the hydrogenated and deodorized oil are provided in Table 7.

Esai Delta Tocopherol, Kalsec rosemary extracts and Eastmas  
 20 GT-2 mixed tocopherols were added to samples from each of  
 the batches. Kalsec refers to the Herbalox product  
 mentioned above. As can be seen from Table 7, the addition  
 of natural antioxidants improves AOM values for Batches 1-  
 3. However, the addition of natural antioxidants,  
 25 especially delta tocopherols, in Batch 3 has a much greater  
 affect in increasing the AOM than does addition in Batches  
 1 and 2. At room temperature, the oil so produced was  
 essentially clear, that is, at room temperature the oil  
 included only small amounts of scattered crystals.

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#### COMPARISON EXAMPLE

Small amounts of natural antioxidants are added to the high  
 oleic canola starting oil of the example, without first  
 35 hydrogenating the oil. Results for Rancimat and AOM tests  
 given in table 8.



TABLE 8

	Additive	Rancimat 130°C	AOM Pass	AOM Fail
	None	0.73	20	25
5	.125% GT-2	2.4	30	35
	.25% GT-2	3.43	30	35
	.1% E-Mix D tocopherol	3.13	30	35
10	.2% E-Mix D tocopherol	4.53	30	35
	.1% Kalsec Type 0	0.97		20
	.2% Kalsec Type 0	1.4		20
15	.4% Kalsec Type 0	2.02	30	35

GT-2= 70% mixed tocopherols

20 E-Mix-D= 80% delta tocopherols

The comparative example shows the small effect which occurs when natural oxidants are added to high oleic canola oil which has not been hydrogenated in accordance with the preferred embodiment of the invention.

CLAIMS

1. A vegetable oil which is visibly clear at 21°C, which has a Mettler drop point of below 15°C and which comprises combined levels of C<sub>16:0</sub> and C<sub>18:0</sub> moieties of under 9% by weight and having a minimum AOM of 250 hours.
2. The vegetable oil of claim 1, wherein the oil is derived from rapeseed.
3. The vegetable oil of claim 1 having a minimum AOM of 350 hours.
4. The vegetable oil of claim 1, wherein the oil is derived from a rapeseed oil having greater than 65% oleic acid residues in its triglycerides.
5. The vegetable oil of claim 1, wherein the oil is derived from a starting oil having greater than about 70% by weight C<sub>18:1</sub> fatty acids.
6. The vegetable oil of claim 1, wherein the oil is derived from a starting oil having a C<sub>18:1</sub> content of from 65-95, a C<sub>18:2</sub> of from 5-20, and a C<sub>18:3</sub> content of from 0.5 to 9, all percentages by weight.
7. A process for preparing a fractionated oil comprising: hydrogenating a starting oil obtained from rapeseed and having greater than about 65% by weight C<sub>18:1</sub> fatty acids to an iodine value of from 85 to 72 and fractionating the oil into an olein fraction and a stearine fraction.
8. The process of claim 7, wherein the starting oil includes less than 70% by weight C<sub>18:3</sub> residues.

9. The process of claim 7, wherein the starting oil has an iodine value of less than 105.
10. A vegetable oil comprising  $C_{18:1}$  moieties at a level of greater than 80% by weight, combined levels of  $C_{16:0}$  and  $C_{18:0}$  of less than 8.5% by weight and an AOM of greater than 150 hours.
11. The vegetable oil of claim 10 derived from rapeseed.
12. The vegetable oil of claim 1 having a Mettler drop point of under  $20^{\circ}\text{C}$ .
13. A process for preparing an oil, comprising:  
hydrogenating a starting oil obtained from rapeseed and having greater than about 65% by weight  $C_{18:1}$  fatty acids and less than 7% by weight  $C_{18:3}$  residues to an iodine value of from about 85 to 75 .
14. The process of claim 13, wherein the starting oil has an iodine value of less than 105.
15. The process according to claim 13, wherein the hydrogenated oil has a melting point below  $18^{\circ}\text{C}$ .
16. A hydrogenated vegetable oil derived from rapeseed comprising triglycerides having 65% or greater oleic acid moieties and an effective amount of a natural antioxidant added thereto to improve oxidative stability.
17. The vegetable oil of claim 16 comprising 800 ppm or greater by wt% of added delta tocopherol.
18. The vegetable oil of claim 16, wherein the natural antioxidant is selected from the group consisting of alpha tocopherol, gamma tocopherol, delta tocopherol and rosemary oleoresin.

19. The vegetable oil of claim 16 having an iodine value of from 85 to 75.
20. The vegetable oil of claim 16 having a  $C_{18:1}$  value of greater than 75% and added delta tocopherol.
21. A process for preparing an oil according to claims 16-20 comprising: hydrogenating a starting oil obtained from rapeseed and having greater than about 65% by weight  $C_{18:1}$  fatty acids to an iodine value of from about 85 to 75 and adding an effective amount of natural antioxidant to improve oxidative stability.
22. Foods made from an oil of claims 1-6, 10-12, or 16-20.

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/EP 93/03566

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 A23D9/00 A23D9/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 5 A23D C11C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,3 804 867 (CPC INTERNATIONAL INC.) 16 April 1974 see column 3; claims 1,3 ---	7
X A	EP,A,0 503 694 (UNILEVER NV) 16 September 1992 see page 2, line 58; claims 1,3-7,11,15,16; examples 1,2 ---	16-19,22 1-3,10, 11,13, 20,21
Y	'TRISUN TECHNICAL BULLETIN HS-500', SVO ENTERPRISES, EASTLAKE, OHIO cited in the application --- -/--	1,3,6,7, 10,13, 14, 16-19, 21,22

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/EP 93/03566

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 326 198 (THE PROCTER & GAMBLE COMPANY) 2 August 1989  see page 4, line 12 - line 13 ---	1,3,6,7, 10,13, 14, 16-19, 21,22
Y	'CANOLA OIL PROPERTIES AND PERFORMANCE NO. 60' October 1982 cited in the application  ---	1,3,6,7, 10,13, 14, 16-19, 21,22
L	JAOCS vol. 67, no. 8 , 1990 pages 487 - 494 K.F. WOLLENBERG 'QUANTITATIVE HIGH RESOLUTION 13C NMR OF THE OLEFINIC AND CARBONYL CARBONS OF EDIBLE VEGETABLE OILS' see page 483; table 3 ---	1,3,6, 10,13,14
A	US,A,2 874 055 (THE BEST FOODS INC.) 17 February 1959  & US,A,24 791 (THE BEST FOODS INC.) 8 March 1960 see claims 5,6; table 3 see column 3 - column 4; table 2 ---	1,4-6, 8-10, 13-15,21
A	WO,A,91 15126 (THE PROCTER & GAMBLE COMPANY) 17 October 1991 see page 13 - page 15, line 15; claims 1,2,6,10,11; examples 4,5 -----	1,2,6, 11,13

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.  
PCT/EP 93/03566

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3804867	16-04-74	NONE	
EP-A-0503694	16-09-92	AU-B- 647889	31-03-94
		AU-A- 1218092	17-09-92
		CA-A- 2062517	12-09-92
EP-A-0326198	02-08-89	US-A- 4948811	14-08-90
		AU-A- 2876289	27-07-89
		JP-A- 2003498	09-01-90
US-A-2874055		NONE	
US-A-24791		NONE	
WO-A-9115126	17-10-91	US-A- 5064670	12-11-91

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